Absorption Line Evaluation Methods for Wavelength Standards

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ABSTRACT

Two methods for absorption line (peak) evaluation based on center of gravity (CG) calculations are described and compared using spectra of the NIST standard reference material (SRM) 1921(a) characterization measurements. These methods are (1) calculating the CG of 50% of the absorption line and (2) an extrapolated center of gravity (ECG) method designed to determine the line minimum (peak maximum) location. Important parameters used in both methods are evaluated. The importance of the spectral data spacing on the accuracy of the CG calculation is examined in detail and quantified for the 1921a lines. The effects of the range of data as well as the fitting routine used in the extrapolation process (in the ECG method) on the final line minimum are examined. A comparison of the absorption line values determined from the SRM 1921(a) spectra by the two methods is presented.

Key words: center of gravity method, peak finding, wavenumber standard, FT-IR, extrapolated peak minimum, extrapolated center of gravity, data spacing, data interval, peak shift, weighted Chi square fit

1. INTRODUCTION

The center of gravity (CG), is an absorption line (peak) evaluation algorithm that has excellent reproducibility (less sensitivity to noise) as well as less sensitivity to spectral resolution, when compared to other evaluation methods that are designed to determine the absorption line minimum (peak maximum) location.[1,2,3] NIST has been using the center of gravity method[1] at a line fraction value, f, of 0.5 (50%) for the calibration values of polystyrene Standard Reference Material (SRM) 1921(a) for calibrating the wavenumber or wavelength scales of spectrometers in the mid-infrared region.[2] Since the line CG value and line minimum values are, by definition, different quantities (except for perfectly symmetrically shaped lines), a direct comparison of values is not readily feasible. To accommodate users who have access only to software which locates the line minimum, we have employed an extrapolated center of gravity (ECG) method, which combines the good features of the CG method with a line minimum locating capability to produce line minimum values for SRM 1921(a). After describing the ECG method in Section 2, an example of its application to the NIST polystyrene SRM 1921(a) measurements is shown in Section 3.

Reference (3) describes the effectiveness of appropriate zero filling to improve peak value determination for spectra measured at lower resolution when the CG ($f = 0.5$) method is used. The next question to ask is: How much zero filling is 'appropriate'? or, equivalently: What is the optimal spectral data spacing? These questions are addressed in Section 4 through a study of the effects of data spacing on the SRM 1921(a) calibrated line values.

2. DESCRIPTION OF THE ECG METHOD

The ECG method is built on the CG calculations. For each absorption line, a series of center of gravity values, v_i, are obtained using the CG method for line fractions f_i ranging from a maximum f_{max} to a minimum f_{min} near $f = 0$. A curve is then fitted to these data and extrapolated to $f = 0$ to obtain the band minimum. Specifically, in this study, for each f_i of a line, an average CG value $\bar{v}_i$ was obtained from 6 measurements of the same sample. To extrapolate to the line minimum, the $\bar{v}_i$ can be fitted by a quadratic curve,

$$V_i = a + bf_i + cf_i^2.$$ (1)

However, to reduce the error in the extrapolation due to noisier data at lower fractions, a chi square (X^2) fit, a curve fit with weighting by the inverse of the standard deviation of the mean, σ_i, of the 6 measurements, was used,[4] where

$$X^2 = \sum \left(\frac{\Delta \overline{V_i}}{\sigma_i}\right)^2 = \sum \left[\frac{1}{\sigma_i^2}\left(\overline{V_i} - a - bf_i - cf_i^2\right)^2\right],$$ (2)

and i refers to the ith line fraction in the series. Setting the derivatives of X^2 in equation (2) with respect to each of the three coefficients, a, b, and c equal to 0 yields three simultaneous equations,

$$\frac{\partial}{\partial a}X^2 = -2\sum \left[\frac{1}{\sigma_i^2}\left(\overline{V_i} - a - bf_i - cf_i^2\right)\right] = 0,$$ (3)

$$\frac{\partial}{\partial b}X^2 = -2\sum \left[\frac{f_i}{\sigma_i^2}\left(\overline{V_i} - a - bf_i - cf_i^2\right)\right] = 0,$$ (4)

and

$$\frac{\partial}{\partial c}X^2 = -2\sum \left[\frac{f_i^2}{\sigma_i^2}\left(\overline{V_i} - a - bf_i - cf_i^2\right)\right] = 0$$ (5)

The extrapolated line minimum, a, is obtained by solving Eqns. (3), (4) and (5) for the coefficients a, b and c.

We now proceed to an example of the ECG method applied to the measurements of polystyrene samples and compare with values obtained from the CG ($f = 0.5$) method.

3. APPLICATION OF THE ECG METHOD

Twelve polystyrene samples were measured sequentially six times (72 measurements in all) under purge using a Bomem DA3 FT-IR spectrometer.[5] The instrumental measurement conditions were: resolution = 0.5 cm⁻¹, aperture diameter = 1 mm, scan speed = 0.5 cm/s, gain = 4, scan number = 100, Hamming apodization, KBr beamsplitter, globar source, and Hg:Cd:Te (MCT) detector. For each polystyrene spectrum the CG values of each of the 13 calibrated line positions were evaluated for line fractions, f, ranging from 0.5 down to 0.05 in 0.05 steps. The original spectrum used for the CG line determination at f = 0.5 had a nominal resolution of 0.5 cm⁻¹ and an exact data spacing of 0.241 cm⁻¹. Since the CG calculation of smaller fractions of a line contains fewer data points than that for f = 0.5, the original interferogram was zero filled 8 times to obtain a data interval of 0.0602 cm⁻¹ in the spectrum (see Section 4 for the discussion of data interval effects). An analysis of the trends of the CG values with line fraction (see Figs. 4 and 5 of reference 3) indicated that CG line value vs. f plots of 13 polystyrene lines can be classified into 3 types. Lines of the first type are those whose line position varies linearly with f; these lines are nominally located at 842, 1154, 1583, 2849 and 3001 cm⁻¹. Lines of the second type are the ones bearing a nonlinear relationship between v and f: the 906, 1601, 3026, 3060 and 3082 cm⁻¹ bands fall into this category. Finally, lines of the third type (545, 1028 and 1069 cm⁻¹) have CG line value vs. f plots which are so irregular that the extrapolated minimum operation must be performed on a reduced range of CG fractions (e.g. $0.01 \le f \le 0.1$).

The specific method selected to handle all three line types properly was to extrapolate to the line minima by applying a 2ⁿᵈ order polynomial fit to the line position average of 6 measurements acquired for each sample, for line fractions in the range of $0.01 \le f \le 0.1$. Plots illustrating this method are shown for four lines in Figure 1. A curve is shown for each of six measurements of one polystyrene sample. In addition, the average value and standard deviation of the mean (error bars), along with the quadratic least squares fit are shown. The fit is extended to $f = 0$ to indicate the minimum position. The
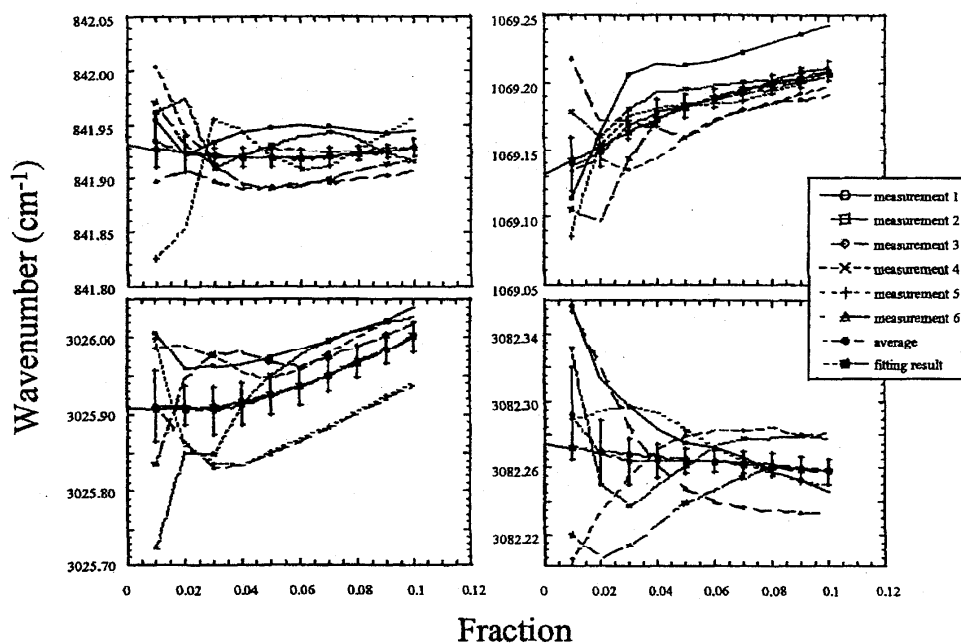
FIGURE 1. The CG line values for 4 bands of polystyrene are plotted as a function of line fraction, f, for 6 individual measurements, along with their average and the quadratic Chi square fit to the average. The Chi square fit is extraploted to $f = 0$ in order to determine the ECG line minimum. In the plots, error bars represent the standard error.

relative effect of spectral noise on the results can be seen as increased variation of measurement-to-measurement results for smaller line fraction values. Hence the necessity of using a fit weighted by the standard deviation of the six measurement

TABLE 1. The results of a weighted 2nd order polynomial X^2 fit for all 13 bands for $0.01 \le f \le 0.1$. All values listed are in cm^{-1}.

peak #	a	b	c	X^2
1	539.871	7.9056	5.9801	0.7726
2	841.933	-0.5214	4.9362	0.1693
3	906.696	0.2125	-0.2501	0.0541
4	1028.092	4.3305	-11.5382	2.4767
5	1069.131	1.3215	-5.4495	0.8955
6	1154.492	-0.7773	7.2399	1.3691
7	1582.974	0.8353	-3.7431	0.0087
8	1601.309	0.0868	2.2829	0.0212
9	2849.364	2.0989	-4.3563	1.0931
10	3001.231	-0.8786	6.7372	0.0209
11	3025.908	-0.2764	12.3979	0.2033
12	3060.025	-0.9499	6.4298	0.1128
13	3082.275	-0.2285	0.6511	0.8235

results. The fitting results of all 13 polystyrene peaks are listed in Table 1, the intercept of the fitting, a, is the extrapolated peak minimum.

The order of polynomial fit is limited to 2nd order to minimize error in the extrapolation to $f = 0$. A comparison was made with results obtained from a 1st order fit. The same set of data was reprocessed by keeping all parameters the same except the fitting order (= 1). The changes in line minima positions ($\Delta a = a_{1st} - a_{2nd}$) for the 1st order fit lie in a very small range from $-0.035 \leq \Delta a \leq 0.0619$ cm^{-1}, while the change inX^2 shows improvement ranging over $0.0133 \leq \Delta X^2 \leq 58.116$. For the 5 lines which have linear line position vs. f relationships, a comparison of the 1st order fit for $0.05 \leq f \leq 0.5$ and the 2nd order fit for $0.01 \leq f \leq 0.1$ reveals similar small changes in Δa of $-0.069 \leq \Delta a \leq 0.030$ cm^{-1} with $-0.124 \leq \Delta X^2 \leq 8.499$, with an exception of the 2849 cm^{-1} band, whose 2nd order X^2 value is 1.093 as compared to a 1st order value of 0.969. The trend of the higher order fit yielding slightly different peak minima with significantly improved regression quality (also shown by F test calculations not discussed) supports the use of quadratic X^2 fitting.

For polystyrene SRM 1921(a) we can compare the results of the CG and ECG methods calculated for a total of 864 measurements on a total of 48 samples. These measurements were made in the same way as those described in Reference (3). The results are shown in Table 2. The mean and standard deviation of all the measurements are shown in columns for each method and for all the calibrated lines. In addition, the differences between the ECG and CG results are shown along with the combination of the standard deviations for comparison purposes. The standard deviation results are obtained from simple statistical calculations and do not represent the final expanded uncertainties[2] to be published at a later date. From Table 2 one can distinguish the symmetrically shaped lines for which the CG and ECG are statistically equal, from those which because of their asymmetrical shape have significantly different values.

TABLE 2. Comparison of CG and ECG results. All values are in cm^{-1}.

CG Results	CG Std. Dev.	ECG Results	ECG Std. Dev.	ECG - CG	Combined Std. Dev.
545.48	1.05	539.91	0.31	-5.57	1.09
842.10	0.30	841.77	0.24	-0.33	0.38
906.86	0.02	906.69	0.05	-0.17	0.05
1028.31	0.06	1028.15	0.05	-0.16	0.08
1069.19	0.18	1069.16	0.17	-0.03	0.25
1154.62	0.02	1154.52	0.04	-0.10	0.04
1583.09	0.04	1583.04	0.04	-0.05	0.06
1601.37	0.03	1601.30	0.02	-0.07	0.03
2850.13	0.03	2849.38	0.06	-0.75	0.06
3001.40	0.02	3001.19	0.05	-0.22	0.06
3026.38	0.03	3025.76	0.12	-0.62	0.12
3060.02	0.02	3059.98	0.05	-0.04	0.05
3082.16	0.04	3082.24	0.06	0.08	0.07

4. STUDY OF DATA SPACING EFFECTS

Zero filling has been used extensively to improve absorption line (peak) location accuracy when using both the CG and ECG algorithms.[3] The results lead one to pose the question of how much zero filling is sufficient to achieve a desired level of accuracy. We present a simple evaluation of this question for a single polystyrene spectrum when using the CG ($f = 0.5$) method. This is done in two parts. We analyze both the effects of changing the data spacing on the wavenumber axis and the effects of changing the data location (for a fixed spacing). We first describe the method for evaluating the effects of data location. This is done by producing a series of spectra that represent all possible ways in which sampling of a continuous spectrum can be performed with a particular data spacing. An analysis of the entire series of spectra will then tell us exactly

how much the calculated line position can vary with where the data points lie on the wavenumber axis. The range of the line position values then represents an uncertainty component to the line position due to the selection of the data spacing and location. Then we perform the same analysis on additional series of spectra, each with a different data spacing. The combined results (shown in Figure 5) answer the question of what data spacing is sufficient.

We begin by generating a quasi-continuous spectrum. An interferogram from a polystyrene sample measurement acquired at resolution = 0.5 cm⁻¹ is zero filled 128 times. The resultant calculated spectrum has a dataspacing as 0.002 cm⁻¹/data point. A program has been written to selectively remove data points from this dense spectrum and generate a series of subsidiary spectra with larger data spacing. To produce a spectrum with a specific data spacing N times larger than the original, the program retains the first data point in the spectrum, the drops the next $N-1$ data points from the spectrum, then retains the next point, then drops $N-1$ more points, etc. until it reaches the end of the spectrum. To generate a complete series for any given N, the process is repeated except that for each additional spectrum the first retained point is shifted by one with respect to the previous spectrum in the series. The spectra continue to be generated until all possible subsidiary spectra are produced. This is illustrated schematically in Figure 2. A synthesized Lorentzian transmission absorption line with data
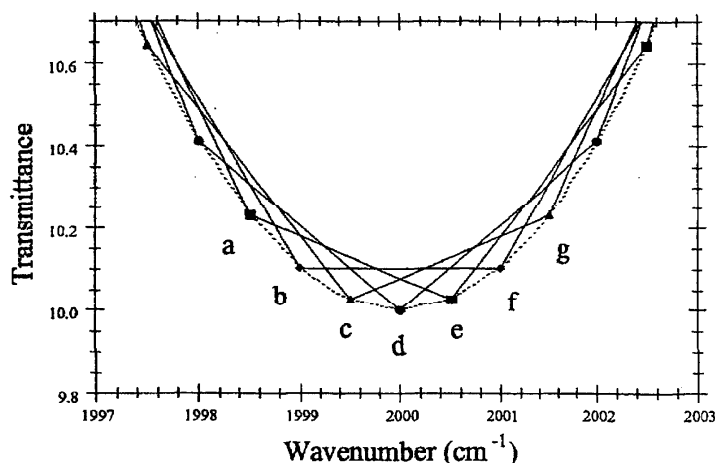

FIGURE 2. Spectra generated through dropping data points in groups of 3 from a synthesized Lorentzian transmission band.

interval of 0.5 cm⁻¹ is shown along with the series of four spectra obtained by dropping data points in sets of 3. The four independent spectra include points a, b, c and d, respectively, while further shifting through points e, f and g produces only degenerate spectra. Thus, removing sets of $N-1$ data points results in N independent spectra.

The data dropping program is then used to generate several series of spectra from the original dense polystyrene spectrum. Ten series of spectra are generated for dropping sets of 50, 100, 150, ... and 500 data points, respectively, from the original spectrum. The ten series contain 51, 101, 151, ... and 501 spectra, respectively (a total of 2760 spectra). Then the CG of each of the 13 calibrated polystyrene absorption lines is evaluated for each spectrum. The data spacing for the ten series are approximately 0.1, 0.2, 0.3, ... and 1.0 cm⁻¹, respectively.

The results for the four series generated with data dropping levels of 100, 200, 300, and 400 for the 906 cm⁻¹ band are shown in Figure 3 as plots of band value versus data location. Both the structure within each curve as well as the trend between curves is qualitatively repeated for all 13 absorption lines. We note the nearly linear behavior between abrupt steps in each curve. We expect to see some variation with data location due to the unavoidable asymmetry in the positioning of the data points with respect to the line center and the weighting of each data point in the CG calculation. Also expected is the increased range of calculated line values with increased data spacing (increased levels of data dropping). For example, the

906 cm^{-1} band shifts in the range of $906.856 \leq \Delta$ cm$^{-1}\leq 906.860$ for a data dropping level of 100 points, and $906.824 \leq \Delta$ cm$^{-1}\leq 906.891$ for a data dropping level of 400 points.
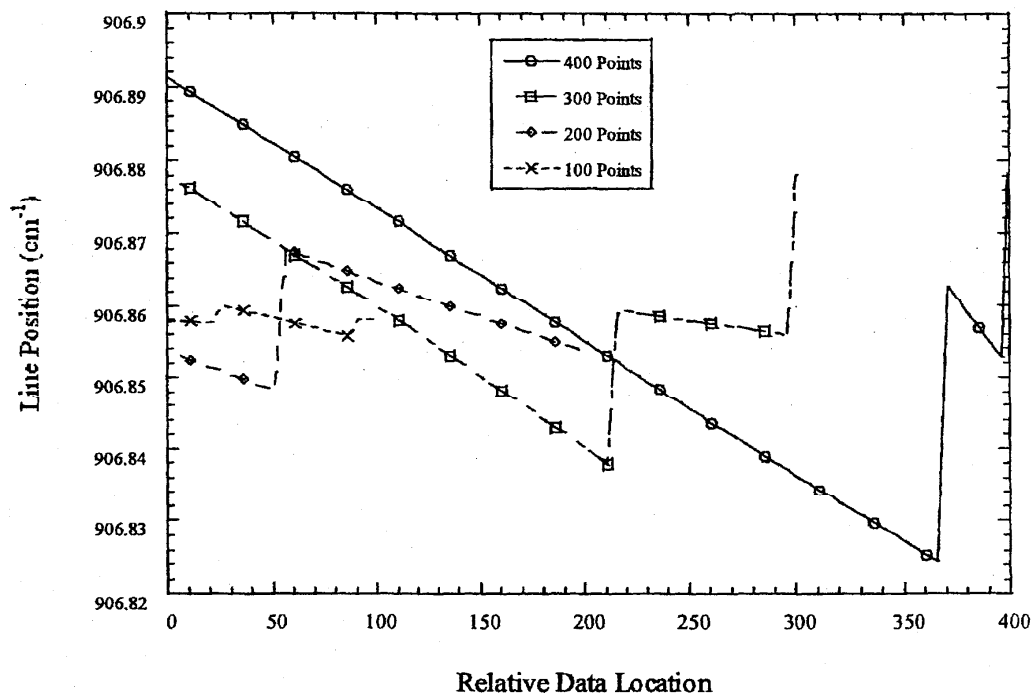

FIGURE 3. Line position shift at different levels of data dropping for the 906 cm^{-1} band for $f = 0.5$. For each level of data dropping, the complete series of spectra are analyzed. Every 5th spectral result is plotted and every 25th is indicated by a symbol on the curves. Each successive spectrum in a series has its data point locations shifted by 0.002 cm^{-1} from the previous spectrum.

A plot of the maximum and minimum line values obtained for each level of data dropping is shown in Figure 4. This figure clearly shows the improvement in the accuracy of the calculation of line value with decreasing data spacing. It can be used to select a particular data spacing for any given level of required uncertainty. For a line which has a very symmetrical structure such as the 906 cm^{-1} band, the distribution of the line maxima and minima values, as seen in Figure 4, is symmetrical about the line value at 0 data drop level (906.858 cm^{-1}). Whereas an asymmetrical band will have an asymmetrical distribution of maxima and minima values. The maximum line shift for any particular level of data dropping we define as the greater of the absolute value of the difference between the line value for 0 data dropping and the (a) maxima and (b) minima line values, respectively.

In Figure 5, the maximum line shift is plotted as a function of data spacing (converted from the data drop level) for every calibrated line of the polystyrene. This summarizes the effects of data spacing on the entire polystyrene spectrum. Two factors primarily affect the size of the effect of data spacing on any line: the degree of asymmetry and width of the line. Since the data points are equally spaced throughout a spectrum, a broad band is represented by more data points than a narrow one.
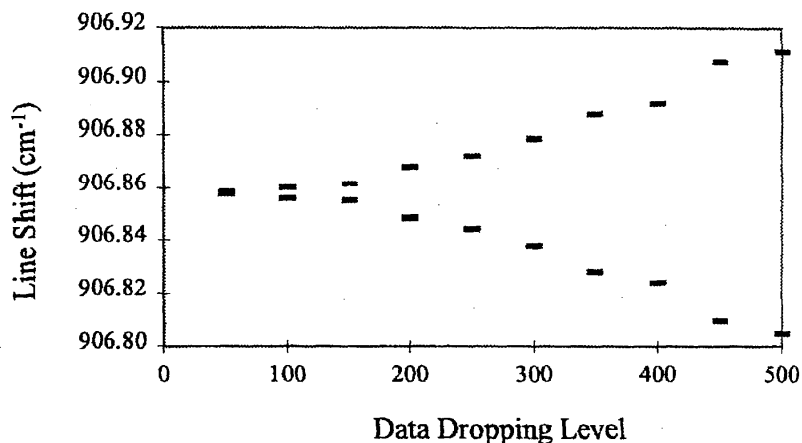
906.92
906.90
906.88
906.86
906.84
906.82
906.80

Line Shift (cm⁻¹)

0   100   200   300   400   500

Data Dropping Level

FIGURE 4. Maximum and minimum line positions for the 907 cm^{-1} band for different levels of data dropping.

So we would expect the broad bands to exhibit smaller shifts in line value for any particular data interval. From the estimated full width at half height (FWHH) listed in the legend of Figure 5, we can see that the narrowest polystyrene line at 1583 cm^{-1} (FWHH = 4.4) has the largest corresponding maximum line shift whereas the broadest line at 545 cm^{-1} (FWHH = 48.1) has the smallest line shift. Hence for evaluation of the entire spectrum, the maximum line shift of the narrowest band is the limiting factor in the selection of the necessary data spacing, and consequently, level of zero filling of the original interferogram.

The results shown in Figure 5 can be used to effectively eliminate any errors from, or at least to estimate the uncertainty components for, the data spacing in the spectra from which CG values are calculated. Many other sources of error can come into play in the measurement from which the spectrum originates. A striking example is the 545 cm^{-1} line, for which, as noted above, the errors due to data spacing effects are negligible. The other sources of error and sample to sample variations result in the largest standard deviation of values from a complete set of measurements of any of the 13 calibrated lines.[3] One of the differences between the CG ($f = 0.5$) and ECG methods is that photometric scale errors can affect the line position value calculated in the CG method, but should only have a minimal effect on the ECG result.

5. CONCLUSIONS AND FUTURE WORKS

We have optimized the procedures used in the CG ($f = 0.5$) and ECG methods for application to the polystyrene wavenumber and wavelength standards. However, the results should be generally applicable for absorption lines with FWHH > the measurement resolution.

A weighted second order polynomial X^2 fit has proven to be an effective way to extrapolate line (peak) minima based on the CG algorithm. The optimal data spacing used to determine the line position by the CG method at $f = 0.5$, depends on the maximum allowable line position uncertainty. For calibration measurements of the polystyrene SRM 1921(a), the data spacing of 0.248 cm^{-1} results in a maximum line position error of < 0.02 cm^{-1} for the narrowest peak. This becomes an insignificant contribution to the expanded uncertainty of the calibration. Near term planned efforts include a study of the effects of data spacing on the ECG line minimum determination as well as an evaluation of the effect of photometric error on the CG and ECG method results. Also, the individual line position error dependencies on data spacing will be generalized by normalization with respect to the line width and an asymmetry factor.
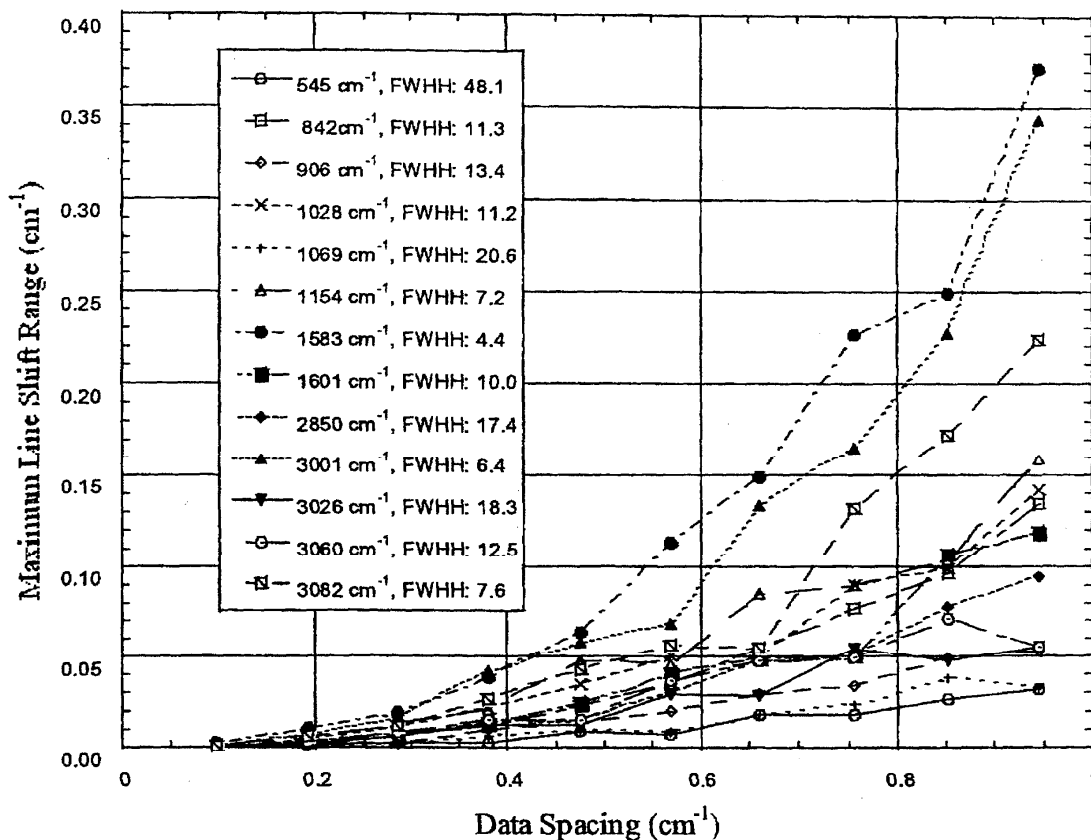
FIGURE 5. Maximum CG line (f = 0.5) shift range for different data densities for all 13 peaks of polystyrene.

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